Vibrational nonequilibrium effects in the conductance of single-molecules with multiple electronic states

R. Härtle, C. Benesch, and M. Thoss

Department of Chemistry, Technical University of Munich,
Lichtenbergstrasse 4, D-85747 Garching, Germany

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Vibrational nonequilibrium effects in charge transport through single-molecule junctions are investigated. Focusing on molecular bridges with multiple electronic states, it is shown that electronic-vibrational coupling triggers a variety of vibronic emission and absorption processes, which influence the conductance properties and mechanical stability of single-molecule junctions profoundly. Employing a master equation and a nonequilibrium Green's function approach, these processes are analyzed in detail for a generic model of a molecular junction and for benzenedibutanethiolate bound to gold electrodes.

Introduction: Charge transport through single-molecule junctions, i.e. molecules which are bound to metal or semiconductor electrodes, represents an interesting and challenging nanoscale nonequilibrium problem. Recent experimental advances have allowed to study the conductance properties of single-molecule junctions and revealed a wealth of intriguing transport phenomena [1, 2, 3, 4]. An important aspect that distinguishes nanoscale molecular conductors from mesoscopic devices is the influence of the nuclear degrees of freedom of the molecular bridge [5, 6, 7]. Due to the small size of molecules, the charging of the molecular bridge is often accompanied by significant changes of the nuclear geometry that indicate strong coupling between electronic and nuclear (in particular vibrational) degrees of freedom [8]. Electronic-vibrational (vibronic) coupling manifests itself in vibrational structures in the conductance, which have been observed for a variety of different systems [5, 6, 9, 10, 11], and may result in current-induced vibrational excitation that destabilizes the junction and causes local heating [12, 13]. Furthermore, conformational changes of the geometry of the conducting molecule are possible mechanisms for switching behavior and negative differential resistance [14, 15]. The physical mechanisms of many of these phenomena, in particular in the resonant transport regime, are not well understood.

In this paper, we investigate vibrational effects in resonant electron transport through single-molecule junctions with multiple electronic states. The basic mechanisms of this nonequilibrium problem are illustrated in Fig. 1. The interaction of a transmitted electron with the vibrational degrees of freedom of the central molecule may result in excitation of vibrational quanta (in the following referred to as emission process, Fig. 1 (a)), or deexcitation (in the following referred to as absorption process, Fig. 1 (b)). For molecular junctions that are dominated by transport through a single electronic state, these basic processes and the resulting conductance properties have been studied in detail employing a variety of theoretical methods including master equations, scattering theory, nonequilibrium Green's function approaches and path integral methods [7, 16, 17, 18, 19, 20, 21, 22, 23].

The situation is considerably more complex if multiple electronic states of the molecular bridge are involved in the transport process. In particular, higher lying electronic states can facilitate deexcitation of the vibrations via resonant absorption processes associated with the sequential transmission of two electrons (Fig. 1 (c)), thus stabilizing the molecular junction. Moreover, vibronic coupling results in an effective interaction of electrons in different electronic states similar to electron-electron coupling in Hubbard-like models. As a result of the intricate interplay of these different processes vibrational and electronic signatures in the conductance of a single molecule may become of the same importance.

Theory: To study vibrationally coupled electron transport in molecular junctions, we consider a single molecule that is covalently bound to two metal leads (L,R) described by the Hamiltonian $H = H_{el} + H_{vib}$. The electronic part of the Hamiltonian,

$$H_{el} = \sum_{i \in M} \epsilon_i c_i^\dagger c_i + \sum_{k \in L,R} \epsilon_k c_k^\dagger c_k + \sum_{k,i} (V_{ki} c_k^\dagger c_i + \text{h.c.}), \quad (1)$$
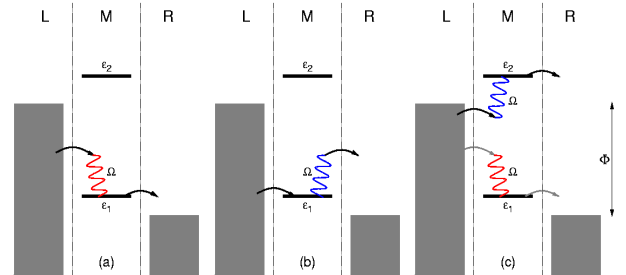

FIG. 1: Schematic representation of vibronic transport processes in a molecular junction involving emission (a) and absorption (b) of vibrational quanta upon transmission of an electron through a single electronic state, as well as emission and subsequent absorption associated with sequential electron transmission via two different electronic states (c).

involves the electronic states of the molecular bridge with energies ϵ_i that are coupled by interaction matrix elements V_{ki} to electronic states in the leads with energies ϵ_k. The vibrational degrees of freedom of the molecular bridge are described by

$$H_{\mathrm{vib}} = \sum_\alpha \Omega_\alpha a_\alpha^\dagger a_\alpha + \sum_{\alpha, i \in \mathrm{M}} \lambda_{i\alpha}(a_\alpha + a_\alpha^\dagger)c_i^\dagger c_i. \quad (2)$$

Here, a_α is the annihilation operator for a vibration with frequency Ω_α, and $\lambda_{i\alpha}$ denote the corresponding vibronic coupling constants.

Several observables are of interest to analyze the interplay of the electronic and vibrational degrees of freedom in nonequilibrium transport through a molecular junction. Here, we consider specifically the current-voltage characteristics $I(\Phi)$ and the vibrational excitation $\langle a_\alpha^\dagger a_\alpha \rangle$. To calculate these observables, we employ two complementary approaches: a nonequilibrium Green's function (NEGF) method [24, 25] as well as a master equation (ME) approach. Briefly, both approaches are based on the small polaron transformation of the Hamiltonian [7], which facilitates a nonperturbative description of vibronic interaction. The transformed Hamiltonian $\overline{H}$ comprises an exactly solvable part $\overline{H}_0$ and a renormalized molecule-lead coupling term $\overline{V} = \sum_{k,i}(V_{ki}X_i c_k^\dagger c_i + \mathrm{h.c.})$, which involves the shift operators $X_i = \exp(\sum_\alpha (\lambda_{i\alpha}/\Omega_\alpha)(a_\alpha - a_\alpha^\dagger))$. It is noted that for models with multiple electronic states $\overline{H}_0$ includes Hubbard-like terms $\sim \lambda_{i\alpha}\lambda_{j\alpha}c_i^\dagger c_i c_j^\dagger c_j$, $i \neq j$, which describe vibrationally mediated electron-electron coupling.

In the ME approach, all observables are obtained from the reduced density matrix ρ of the electronic and vibrational degrees of freedom of the molecule, which is given as the stationary limit of the well-established equation of motion [17, 19]

$$0 = -i\left[\overline{H}_0, \rho\right] - \int_0^\infty \mathrm{d}\tau \, \mathrm{tr}_{\mathrm{leads}}\left\{\left[\overline{V}, \left[\overline{V}(\tau), \rho\,\rho_{\mathrm{leads}}^{\mathrm{eq}}\right]\right]\right\}. (3)$$

Here, $\rho_{\mathrm{leads}}^{\mathrm{eq}}$ denotes the equilibrium density matrix of the leads. In the results reported below, electronic coherences of the density matrix ρ are fully taken into account, while vibrational coherences are negligible. The current is given by $I = (2e/\hbar)\int_0^\infty \mathrm{d}\tau \, \mathrm{tr}\{[\overline{V}(\tau), \rho\rho_{\mathrm{leads}}^{\mathrm{eq}}]\hat{I}\}$, with $\hat{I} = \sum_{i,k \in \mathrm{L}}(V_{ki}c_k^\dagger c_i X_i - \mathrm{h.c.})$ and $\overline{V}(\tau) = \mathrm{e}^{-i\overline{H}_0\tau}V\mathrm{e}^{i\overline{H}_0\tau}$.

The NEGF method is an extension of the approach outlined in Refs. 24, 25 to treat multiple electronic states. Thereby, the electronic Green's function matrix $\mathbf{G}$ is determined by the self energy matrix $\mathbf{\Sigma}_{\mathrm{L/R},ij}(\tau, \tau') = \sum_{k \in \mathrm{L/R}} V_{ki}^* V_{kj} g_k(\tau, \tau')\langle \mathrm{T}_c X_j(\tau')X_i^\dagger(\tau)\rangle$, where g_k denotes the free Green's function of lead state k and T_c denotes time-ordering on the Keldysh contour. Vibrationally induced electron-electron interaction is treated non-perturbatively following the strategy of Ref. 26. The calculation of the correlation functions $\langle \mathrm{T}_c X_j(\tau')X_i^\dagger(\tau)\rangle$ is based on a cumulant expansion in the dimensionless coupling parameters $\lambda_{i\alpha}/\Omega_\alpha$, which in turn involves

the electronic Green's function and, therefore, is obtained in a self-consistent scheme [24, 25]. Within the NEGF method, the current is given by $I = (2e/\hbar)\int (\mathrm{d}E/(2\pi)) \, \mathrm{tr}\{\mathbf{\Sigma}_{\mathrm{L}}^< \mathbf{G}^> - \mathbf{\Sigma}_{\mathrm{L}}^> \mathbf{G}^<\}$.

In both approaches the molecule-lead coupling is treated within (self-consistent) second order perturbation theory. The ME approach includes all resonant processes, however, it neglects contributions related to co-tunneling, and does not account for the broadening of the electronic levels induced by the interactions with the leads. These processes are taken into account in the NEGF method [24, 25], which, as a result, becomes exact for vanishing vibronic coupling. On the other hand, the ME approach allows an exact treatment of the Hubbard-like terms in $\overline{H}_0$, while these are approximately accounted for in the NEGF method. Thus, both approaches are complementary and the good agreement of the results found below is a strong indication of their validity.

Results: First, we consider a generic model system for a molecular junction, represented by two electronic levels and a single vibrational mode with frequency Ω=0.1 eV. Both leads are modeled by semi-elliptic bands [18] with a band width of 3 eV and an overall molecule-lead coupling strength of 0.1 eV. Throughout this article, we consider a low temperature of $T = 10$ K to ensure that vibrational excitation is caused solely by nonequilibrium processes.

Fig. 2 shows the current-voltage characteristic and the average vibrational excitation for a moderate vibronic coupling, $\lambda_{1/2}$=0.06 eV, obtained with the ME approach. The first electronic level is located at ϵ_1=0.15 eV (relative to the Fermi energy of the leads) and we consider two different locations of the second electronic level, ϵ_2.

As a reference, also the result for a single electronic level at ϵ_1 is shown. For the latter result, the molecule-lead coupling has been enhanced by a factor $\sqrt{2}$ to obtain the same current as in the two-level cases for large voltages. Overall, the interaction of the transmitted electrons with the vibration results in pronounced vibronic resonance structures in the current-voltage characteristic and significant vibrational excitation. As has been previously studied in detail for a single electronic level [24, 25], the current exhibits a steplike increase at voltages $\Phi \approx 2(\epsilon_1 - \lambda_1^2/\Omega + n\Omega)$, $n = 0, 1, 2, ...$ The corresponding current-induced vibrational excitation also shows a step-like monotonous increase with voltage, and acquires considerable values.

The situation becomes significantly more complex if another electronic level participates in the transport process. In the current voltage-characteristic, this results in a wealth of additional resonance structures. Due to vibrationally induced electron-electron interaction, the resonance, which for a purely electronic transport mechanism would appear at $\Phi \approx 2\epsilon_2$, splits into two resonances at $\Phi \approx 2(\epsilon_2 - \lambda_2^2/\Omega)$ and $\Phi \approx 2(\epsilon_2 - (\lambda_2^2 + 2\lambda_1\lambda_2)^2/\Omega)$ (indicated by the dashed lines in Fig. 2). They correspond to the first electronically excited state of the anion and the electronic ground state of the di-anion, respectively [27]. Vibrational progressions originating from all three elec-
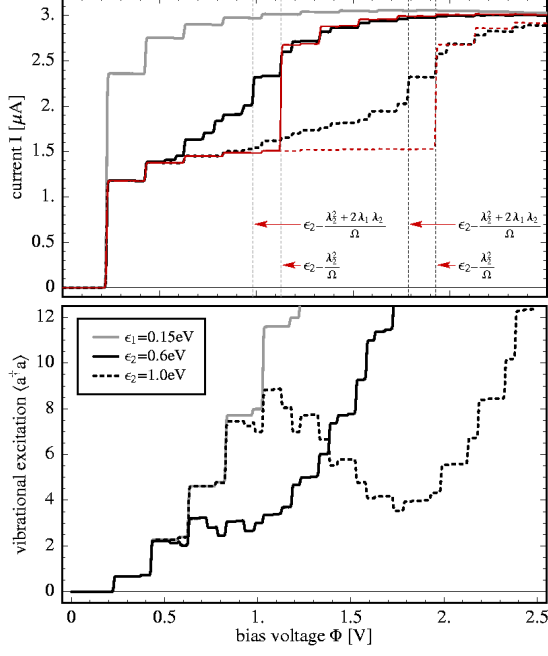
FIG. 2: Current and vibrational excitation for a generic
model system with two electronic levels and a single vibra-
tional mode obtained for two different locations of the second
electronic state. The red lines depict results of an approxi-
mate treatment where the current through the two electronic
states has been calculated separately and the grey lines give
results for a single electronic state.

FIG. 3: Current and vibrational excitation for a generic
model system with two electronic states, ϵ_1=0.15 eV and
ϵ_2=0.6 eV, and different vibronic coupling parameters as in-
dicated in the legend.

tronic resonances towards higher voltages can be seen.
An intriguing effect is the appearance of pronounced vi-
bronic resonance structures at lower voltages, where the
electronic level ϵ_2 is still outside the conductance window.
These structures are related to the absorption processes
schematically depicted in Fig. 1(c): Upon transmission
via the lower lying electronic resonance ϵ_1, an electron
may excite vibrational quanta. A subsequently trans-
mitted electron can absorb these quanta, thus effectively
lowering the energy of the resonances. This results in
vibronic structures at voltages $\Phi \approx 2(\epsilon_2 - \lambda_2^2/\Omega - n\Omega)$
and $\Phi \approx 2(\epsilon_2 - (\lambda_2^2 + 2\lambda_1\lambda_2)^2/\Omega - n\Omega)$, $n = 0, 1, 2, ...$ As
a consequence of the additional vibronic structures, the
purely electronic resonance steps are barely visible. We
emphasize that this resonant absorption process is a col-
lective effect of the two electronic states and cannot be
described in an approximate treatment, which calculates
the currents through the two electronic levels separately
(red lines in Fig. 2).

The absorption of current-induced vibrational energy
via higher-lying electronic states has an even more pro-
nounced effect on the vibrational nonequilibrium distri-
bution in the stationary state. The results in Fig. 2
demonstrate that this process may reduce the vibrational
energy by more than 50%. Thus, higher lying electronic
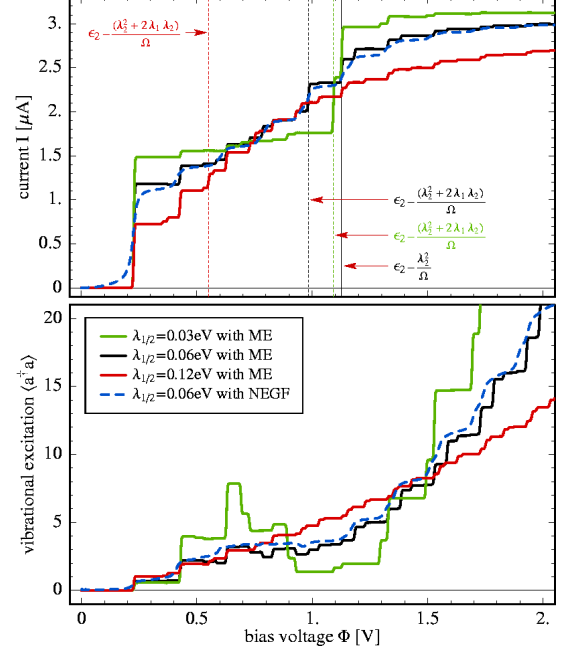levels stabilize single-molecule junctions with respect to

local heating.

Another interesting aspect is the influence of the vi-
bronic coupling strength $\lambda_{1/2}$. Fig. 3 shows results ob-
tained for the two-state model considered above, but dif-
ferent vibronic coupling parameters. Thereby, the ener-
gies of the electronic states $\epsilon_{1/2}$ have been adjusted to
compensate for the different polaron shifts, $\lambda_{1/2}^2/\Omega$. In
the current-voltage characteristic, a larger vibronic cou-
pling results in more pronounced vibrational step struc-
tures. The results obtained for the vibrational excitation
show that, except for regions with resonant absorption,
the largest current-induced vibrational excitation is ob-
tained for the system with the weakest vibronic coupling.
This counterintuitive behavior has been analyzed before
for the case of a single electronic state [21, 22]. In par-
ticular, it has been shown that the vibrational excitation
diverges in the limit $\lambda\to0$ if no other vibrational relax-
ation processes are active. The present results demon-
strate that this vibrational instability can be considered
as an 'artifact' of the restriction to a single electronic
level on the molecule. Vibrational absorption processes
related to higher-lying electronic states, which will al-
ways be present in a real molecule, limit the vibrational
excitation, and thus, prevent this instability.

The comparison of results obtained with the ME ap-
proach and NEGF theory in Fig. 3 reveals very good
agreement for small (data not shown) and moderate vi-
bronic coupling, and thus, indicates the validity of the
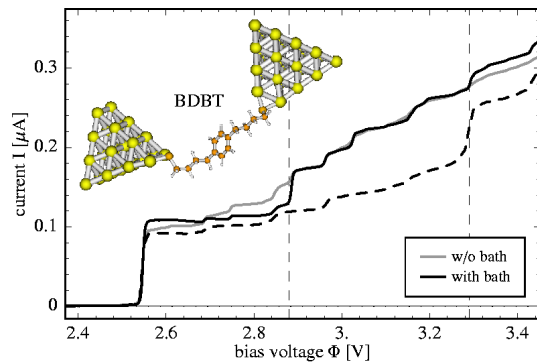two approaches. The only major difference is the broad-

FIG. 4: Current-voltage characteristic for a BDBT molecular junction, with and without coupling to a bath. The dashed line depicts results of an approximate treatment [24], where the current through the two electronic states has been calculated separately.

ening of the step structures due to tunneling processes. For strong vibronic coupling, e.g. $\lambda_{1/2} = 0.12$ eV, the NEGF approach ceases to be valid due to the cumulant expansion employed [24, 25].

The results discussed so far were obtained for a generic model system of a molecular junction. Finally, we consider vibrational nonequilibrium effects in electron transport through a realistic molecular junction, where a p-benzene-di(butanethiolate) molecule (BDBT) is covalently bound to two gold electrodes. Recent first-principle electronic structure calculations for this system have shown that the transport properties of this junction can be well represented by a model that includes two electronic states, localized on the molecular bridge, and four vibrational modes [28]. The influence of the remaining vibrational degrees of freedom of the molecule and the phonons of the gold electrodes are represented by a coupling to a bath as described in Ref. 24. It is noted that, in contrast to the generic model discussed above, the two molecular levels that dominate charge transport through BDBT are occupied in equilibrium, and thus, the prevailing mechanism is hole transport. Correspondingly, the electronic-vibrational coupling term in Eq. 2 is replaced by $\sum_{\alpha, i \in M}(-\lambda_{i\alpha})(a_\alpha + a_\alpha^\dagger)c_i c_i^\dagger$.

Fig. 4 shows the respective current-voltage characteristics using NEGF theory. Similar as for the model system discussed above, the presence of two vibrationally-coupled electronic states results in a splitting of the resonance corresponding to the lower electronic state into two step structures (indicated by the dashed vertical lines). The vibronic coupling causes significant current-induced vibrational excitation and manifests itself in the current-voltage characteristic in a wealth of vibrational structures due to emission and absorption processes. As a consequence, electronic and vibrational features are hardly distinguishable. This scenario might be very common for realistic molecular junctions, which typically involve many active vibrational modes. If the coupling to the bath is included (solid black line), vibrational relaxation processes compete with current-induced excitation resulting in an overall smaller vibrational excitation. As a consequence, resonant absorption processes are less important and electronic resonances in the current-voltage characteristic are more pronounced.

Conclusions: Processes due to electronic-vibrational coupling can influence the conductance properties and mechanical stability of single-molecule junctions profoundly. The results presented in this paper demonstrate that in molecular junctions where multiple electronic states participate in the nonequilibrium transport, a number of additional vibronic processes have to be considered. These include, in particular, resonant absorption processes associated with the sequential transmission of two electrons as well as vibrationally induced effective electron-electron interaction. While the latter results in a splitting of electronic resonances, the former may cause a wealth of additional vibronic structures in the current-voltage characteristic. Moreover, the resonant absorption process facilitates vibrational cooling and thus represents an important stabilization mechanism of molecular junctions. Since polyatomic molecules include numerous vibrational modes and often exhibit multiple closely-lying electronic states, these findings are expected to be of relevance for most molecular junctions.

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